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**SYNTHESIS AND PROPERTIES OF RODLIKE
AROMATIC HETEROCYCLIC POLYMERS:
PHENYLATED PARA-TERPHENYLENE-POLYBENZOBIS-
OXAZOLES**

*POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION*

DECEMBER 1978

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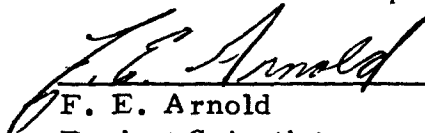
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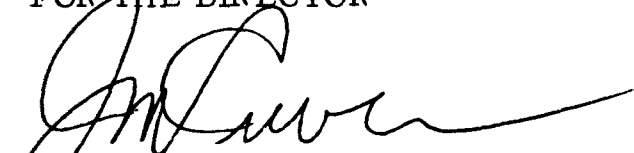
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the range of 2.5 to 9.3 dl/g. The solubility and thermal stability of the phenylated polymers are improved when compared with the nonphenylated analog.

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q4 Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFML Project Scientist. Co-authors were Dr. J. F. Wolfe (Visiting Scientist) and Dr. F. E. Arnold, Air Force Materials Laboratory, (AFML/MBP).

This report covers research conducted from April 1976 to January 1978.

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SECTION I

INTRODUCTION

One of the goals of current synthetic polymer research is to prepare high-modulus, high-strength structural materials for aerospace applications. The successful polymer system must

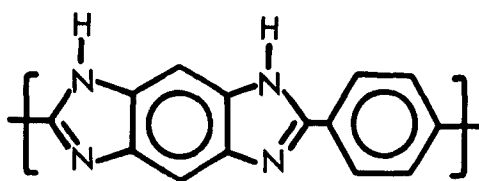
- (1) Have a molecular structure that imparts unusually high tensile strength and modulus
- (2) Be amenable to fabrication by a method that maximizes these properties
- (3) Possess a high use-temperature
- (4) Result in moisture-insensitive and hydrolytically stable fabricated parts.

A number of aromatic polyamide and poly(amide hydrazide) fibers recently described in the literature¹⁻⁴ meet the first two of these criteria. The overriding structural feature of these materials is a highly chain-extended or rodlike configuration in solution. This structure is a result of both the para-phenylene units and the partial double bond character of the carbon-nitrogen bond in predominately trans-amide linkages. The realization of the extremely high modulus and strength, however, is a result of their solubility in a suitable solvent at which molecular ordering occurs above a threshold concentration. These anisotropic solutions are then spun and drawn to give a highly ordered morphology. Although these high-modulus/high-strength fibers have important and widespread applications as reinforcements below 200°C, they do not meet the use-temperature or hydrolytic stability at elevated temperatures required for advanced aerospace applications.

The high use-temperature requirement (300°C or higher) limits the possible molecular structure of an organic polymer to an all-aromatic

heterocyclic backbone. All pendant groups must also be aromatic to avoid eventual oxidation of the backbone. High phase transition temperatures, T_g and T_m , as well as a high degree of thermo-oxidative stability are essential. The required high T_g , in turn, limits the feasible processing methods to solution techniques. The overall goal of this research, therefore, is to prepare an all-aromatic rodlike polymer that forms anisotropic solutions in a convenient solvent.

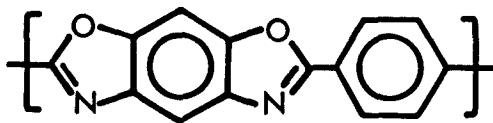
The all-parabenzobisimidazole polymer I meets the above thermal requirements



I

and possesses the required rodlike structure. Polymer I of high molecular weight⁵ showed strong birefringence under crossed polars, stir-opalescence in concentrated methanesulfonic acid solution, and the tendency to form aggregated films in the solid state similar to the rodlike ladder polymer BBL.⁶ However, I was soluble only in methanesulfonic acid and showed deleterious levels of moisture absorption.

A structural analog of polymer I, the benzobisoxazole polymer IIa, has been prepared⁷ and anisotropic solutions



IIa

have been formed in methanesulfonic acid.⁸ Polymer IIa showed no moisture sensitivity, but was also soluble only in strong mineral acids and strong Lewis acids. Attempts are being made to prepare high modulus, high strength fibers from anisotropic solutions of polymer IIa in methanesulfonic acid.⁹

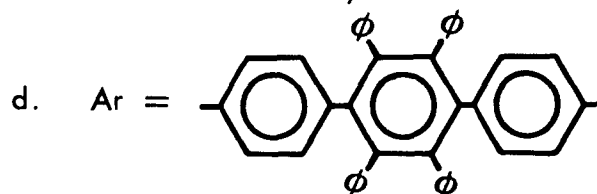
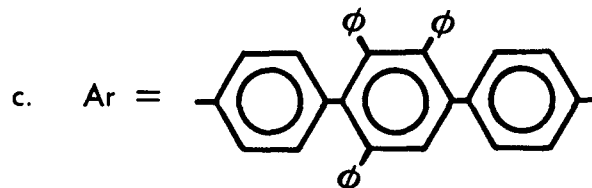
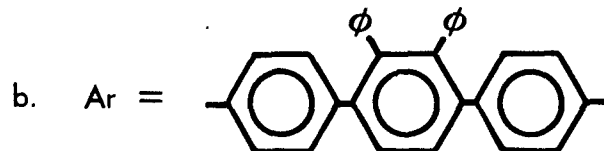
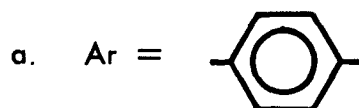
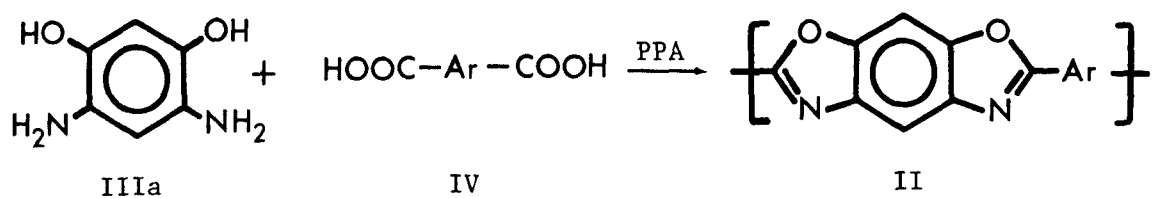
The solubility of a number of relatively flexible aromatic polymers with pendant phenyl groups, such as the polyphenylquinoxalines¹⁰ or phenylated polyphenylenes,¹¹ is increased when compared with their nonphenylated analogs. The solubility increase is presumed to result from a modification of chain packing, which allows greater solvent-polymer interaction and increases the distance between adjacent chains.

This report describes an effort to synthesize all-para polybenzobisoxazoles with pendant phenyl groups on the backbone with the objective of increasing the number of suitable processing solvents while maintaining the rodlike structure of the polymer.

SECTION II

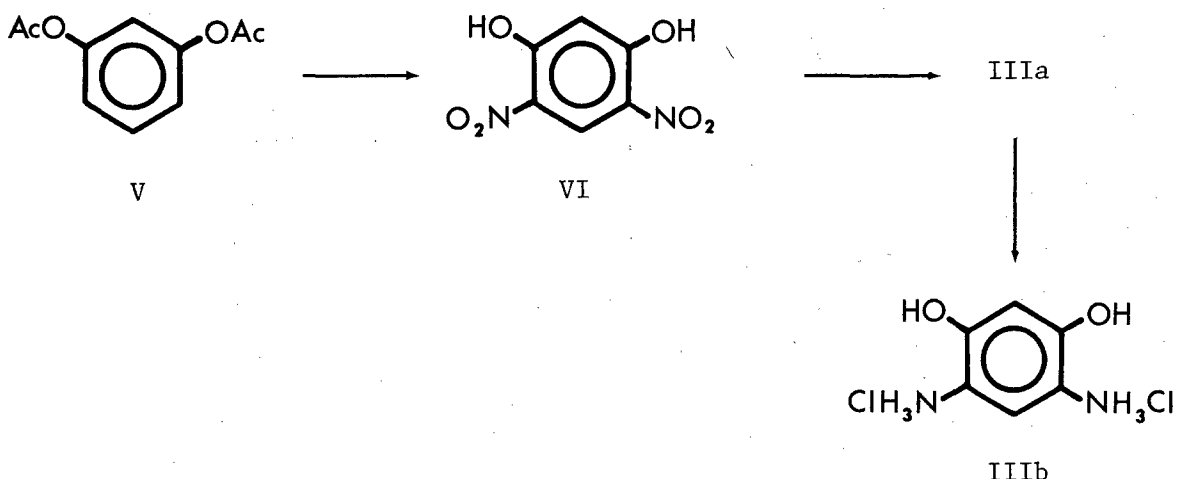
RESULTS AND DISCUSSIONS

Rodlike polymers IIb-d containing alternating benzo [1,2-d:5,4-d'] - bisoxazole and para- aromatic moieties were prepared by the in situ generation of 4,6-diaminoresorcinol (IIIa) from its dihydrochloride salt (IIIb) in polyphosphoric acid (PPA) followed by condensation with various aromatic para-dicarboxylic acids (IVb-d) at elevated temperature.



A. Monomer Syntheses

Monomer IIIb was prepared by the dinitration of diacetyl resorcinol (V), hydrolysis of V to 4,6-dinitroresorcinol (VI), and catalytic hydrogenation of VI to give IIIa.

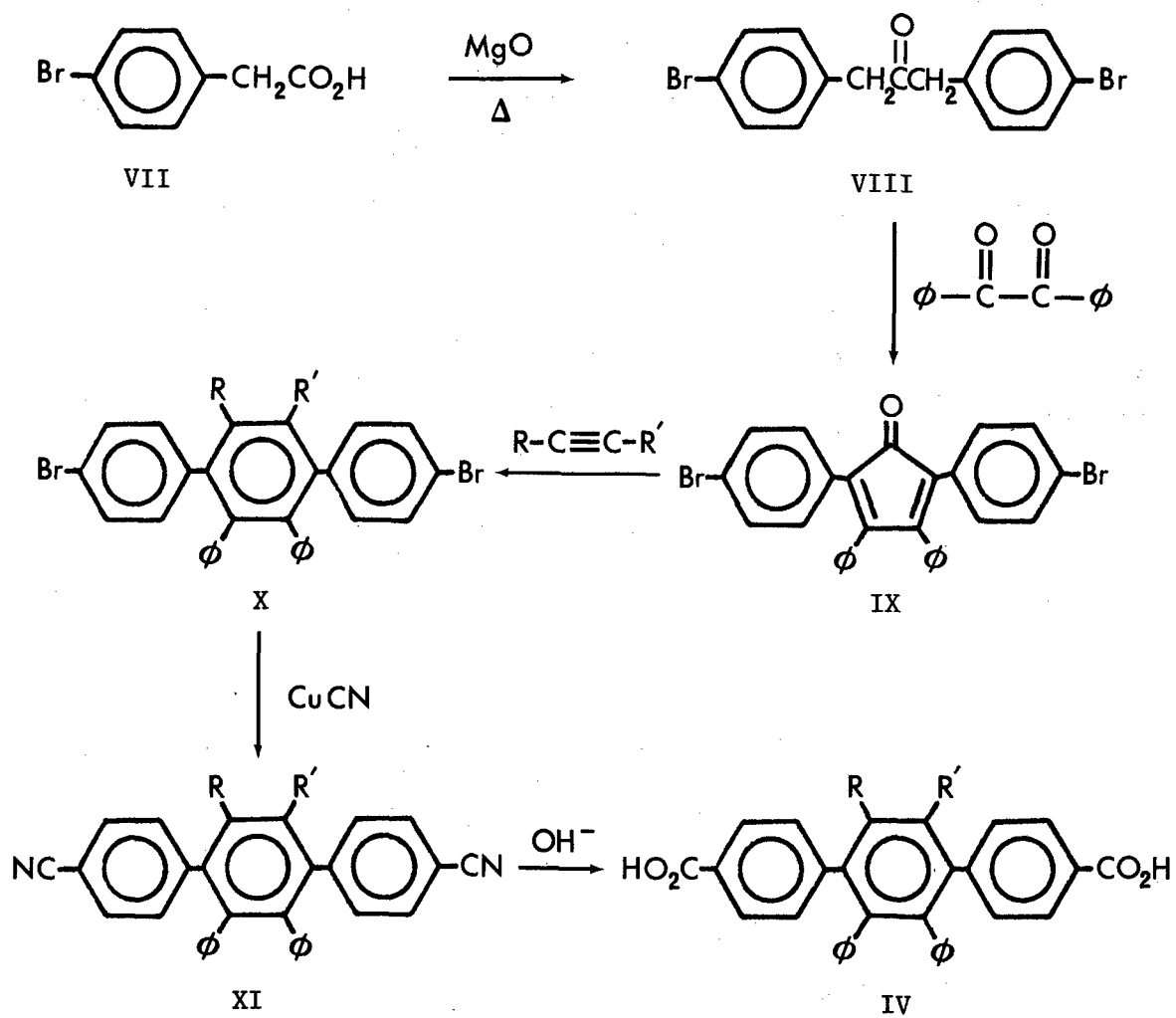


The monomer was isolated as the dihydrochloride salt IIIb by precipitation of the hydrogenation mixture into tetrahydrofuran that had been saturated with gaseous hydrogen chloride. The air-sensitive IIIb was recrystallized in aqueous stannous chloride/hydrochloric acid to give colorless platelets that could be weighed in air without noticeable decomposition.

The aromatic para-dicarboxylic acids IVb-d used in this study were prepared by the following scheme:

When an intimate mixture of *p*-bromophenylacetic acid (VII) and magnesium oxide was heated to 340°C under reduced pressure, 1,3-bis(*p*-bromophenyl)-2 propanone (VIII) was collected in 70% yield by distillation. Condensation of VIII with benzil in ethanolic potassium hydroxide gave 2,5-bis(*p*-bromophenyl)-3,4-diphenylcyclopentadienon (IX) in 93% yield. The Diels-Alder reactions of IX with norbornadiene at 110°C, phenylacetylene at 139°C, and diphenylacetylene at 305°C gave the 4,4''-dibromophenylated-*p*-terphenyl compounds Xb, Xc, and Xd, respectively, in yields of >90%. These reactions were easily monitored visually because of the loss of the dark purple color of IX. The nucleophilic displacement of the bromo groups by cuprous cyanide in dry *N*-methyl-2-pyrrolidinone (NMP) gave the dicyano intermediates XIb-d in yields of 65 to 96%. The use of dry NMP increased the yield and decreased the amount of hydrolyzed cyano groups and thus facilitated purification of XI, which in turn increased the purity of IV. Hydrolysis of XIb-d in alkaline ethylene glycol gave the dipotassium salt of monomers IVg-d, which crystallized directly from the hydrolysis mixture. Acidification of the purified salt gave monomers IVb-d in yields of 60 to 70%.

The diacid monomers IVb-d are white solids that are thermally stable up to their melting points of 425°C, 425°C, and 450°C, respectively, as shown by differential scanning calorimetry (DSC).

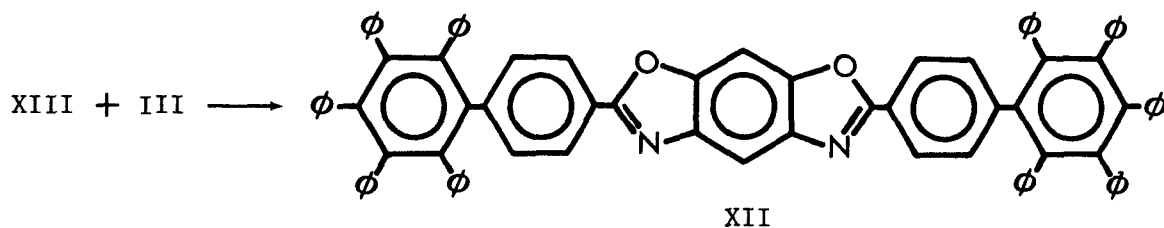


b. $R = R' = H$

c. $R = C_6H_5, R' = H$

d. $R = R' = C_6H_5$

The model compound XII, 2,6-bis(2, '3, '5, '6, '-tetraphenyl-p-terphenyl) benzo [1,2-d:5, -4d'] bisoxazole, was prepared in 87% yield by the reaction of 4,6-diaminoresorcinol (IIIa) and p-(pentaphenyl-phenyl) benzoic acid (XIII) in a mixture of PPA/sulfolane. The acid XIII was prepared by the Diels-Adler reaction of p-(phenylethynyl)-benzoic acid¹² (XIV) and tetraphenylcyclopentadienone (XV).



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C. Polymer Syntheses

Polymer IIa, poly{[benzo(1,2-d:5,4-d')bisoxazole-2,6-diyl]-1,4-phenylene}, was synthesized previously⁷ by gently heating a stoichiometric mixture of IIIb and terephthalic acid in freshly prepared PPA until dehydrochlorination was complete, and then slowly heating the mixture to a maximum temperature of 200°C. This procedure yielded polymers with intrinsic viscosities in methanesulfonic acid at 30°C in the range of 2.8 to 3.7 dl/g. Attempts to polymerize III and IVb-d by this procedure failed because of the insolubility of IVb-d. Monomers IVb-d were, however, partially soluble in sulfolane at 120°C. A modified procedure was therefore adopted by which IIIb was slowly heated to 90°C in PPA to effect dehydrochlorination and then a stoichiometric amount of finely powdered monomer IVb, c, or d was added at 120°C as a slurry in sulfolane.

The polymerization mixture became homogenous at various temperatures depending on which diacid monomer IV was used, on the monomer concentration, and on the PPA/sulfolane ratio. The solubility of IV in a 1/1 mixture of PPA/sulfolane was IVb>IVc>IVd. The monomer solubility increased with decreasing PPA/sulfolane ratio, but the polymer solubility decreased. Therefore, monomer concentration could be increased to 1.5% for scale-up purposes by decreasing the PPA/sulfolane ratio from 1 to 0.77. Higher monomer concentrations resulted in formation of insoluble polymer due to incomplete solubility of monomer IV.

Copolymers of the di-, tri-, and tetraphenylated diacids IVb-d with monomer III were prepared in PPA/sulfolane. Insoluble polymer was obtained in one run due to incomplete dissolution of the tetraphenylated diacid IVd. The insolubility is presumed to result from crosslinks formed when the unreacted o-aminophenol end groups decompose at elevated temperature.

Ease of dehydrochlorination of monomer IIIb in PPA depended on concentration. At concentrations near 0.5%, the reaction was heated to about 80°C, which decreased the viscosity of the PPA and facilitated the release of the release of the bubbles of hydrogen chloride. If the concentration was increased to 2% monomer in PPA, any heating above room temperature caused uncontrollable foaming. Hydrogen chloride evolution was thus hindered by the high viscosity of the medium at room temperature.

D. Polymer Solubility

The solubility of the phenylated polymers IIb-d showed a marked improvement over that of the nonphenylated polymer IIa. Whereas IIa precipitated from the 1/1 PPA /sulfolane polymerization mixture as a low-molecular-weight oligomer, polymers IIb-d remained in solution to high molecular weight. Polymer IIa was soluble only in strong acids, whereas polymer IIc is soluble in methanesulfonic acid and benzenesulfonic acid and in mixtures of dichloroacetic acid/m-cresol (50/50), of formic acid/m-cresol (30/70), of dichloroacetic acid/methanesulfonic acid (10/10). Concentrated solution properties will be determined in a future effort to evaluate the potential of the polymers as high-strength, high modulus materials.

The solubility characteristics of these polymers may be altered by inverse precipitation. A sample of IIc that was isolated by precipitation into methanol and then simply washed thoroughly had an intrinsic viscosity in methanesulfonic acid of 9.3 dl/g. After dissolution in methanesulfonic acid and precipitation by slow addition of methanol, the polymer had an intrinsic viscosity in the same solvent of 3.8 dl/g. This behavior can be explained by the existence of stable molecular aggregates that form as the polymer is precipitated slowly, thus giving them enough time to orient. These aggregates are

visualized as lengthwise oriented bundles of rods of a few molecules in size and do not dissociate when redissolved in the solvent. The lower viscosity is a consequence of the lesser dependence of viscosity on diameter versus length of these bundles. The overriding factor, therefore, becomes the number of bundles. Polymer IIc formed a finely divided solid when inversely precipitated and showed the same tendency to form surprisingly strong films by aggregation of these solid particles as does the rodlike ladder polymer BBL.⁶

E. Thermal Evaluation

The thermal properties of the polymers were evaluated using thermogravimetric analysis (TGA) and isothermal aging. A typical TGA trace for the phenylated system is shown in Figure 1 for polymer IIc and compared to the nonphenylated system IIa. A comparison of the two polymers by isothermal aging is shown in Figure 2 at 316°C and 371°C. Isothermal aging studies in air were carried out on polymers with comparable particle size at a flow rate of 40 cc/min. A marked improvement in thermo-oxidative stability of the phenylated polymers was shown by both TGA and isothermal aging at 316°C. This difference could arise from molecular weight differences or the amount of molecular ordering in the samples, but we suspect that the pendant phenyl groups exert an umbrella effect protecting the heterocyclic ring from oxidation. It is interesting to note that at higher temperatures, 371°C, the nonphenylated polymer IIa exhibited better thermo-oxidative stability than the phenylated system, which most likely can be attributed to the loss of the pendant phenyl groups from the later system.

SECTION III

EXPERIMENTAL

Monomers

4,6-Diaminoresorcinol dihydrochloride (IIIb)

A mixture of 4,6-dinitroresorcinol (10.0 g, 0.050 mole), 10% palladium on charcoal (1.0 g), and 10% hydrochloric acid (275 ml) was shaken under 50 psi of hydrogen at room temperature for 24 hrs. The mixture was then filtered through a Celite pad into 1 liter of tetrahydrofuran that had been saturated with gaseous hydrogen chloride. The resulting pink crystals were recrystallized from hot deoxygenated water containing 3% stannous chloride by adding an equal volume of concentrated hydrochloric acid. The colorless crystals were filtered, washed with concentrated hydrochloric acid and ether, and then dried at 60°C/0.1 torr for 6 hr. Mass spectrum (70 eV) m/e 140 (M-2HCl).

Anal. Calcd for $C_6H_{10}Cl_2N_2O_2$: C, 33.82%; H, 4.73%; N, 13.15%; Cl, 33.28%. Found: C, 33.64%; H, 4.90%; N, 13.20%; Cl, 32.10%.

1,3-Bis(p-bromophenyl)-2-propanone (VIII)

An intimate mixture of p-bromophenylacetic acid (323 g, 1.50 mole) and 94% magnesium oxide (66.5 g, 1.65 mole) was heated at 250°C under reduced pressure to remove the water of condensation. Raising the temperature of 340°C at 1 to 3 torr caused distillation of VIII (225 g, 81.6%). Recrystallization from ethanol gave 192 g (70%) of VIII as colorless platelets; mp 120 to 122°C (lit¹³ mp 121 to 122°C).

2,5-Bis(p-bromophenyl)-3,4-diphenylcyclopentadienone (IX)

This intermediate was prepared by the condensation of benzil with VIII, as described in reference 13.

4,4''-Dibromo-2,'3'-diphenyl-p-terphenyl (Xb)

A mixture of IX (190 g, 0.35 mole) bicyc.o [2.2.1] hepta-2,5-diene (370 g, 4.0 mole), and toluene (1 liter) was heated under reflux until the color faded to pink (3 hr.). The solution was cooled in an ice-water bath and the resultant pink crystals collected, washed with methanol, and air dried. Yield: 150 g (80%); mp 275-278°C.

Anal. Calcd for $C_{30}H_{20}Br_2$: C, 66.68%; H, 3.73%. Found: C, 65.95%; H, 3.95%.

4,4''-Dibromo-2,'3,'5'-triphenyl-p-terphenyl (Xc)

A mixture of IX (120 g, 0.22 mole), phenylacetylene (56 g. 0.55 mole), and o-dichlorobenzene (925 ml) was heated under reflux for 2 hr. The yellow solution was poured into methanol (3 liters) to give 127 g (93%) of Xc: mp 273-275°C.

Anal. Calcd for $C_{36}H_{24}Br_2$: C, 70.15%; H, 3.92%; Br, 25.93%. Found: C, 70.67%; H, 4.08%; Br, 25.52%.

4,4''-Dibromo-2,'3,'5,'6'-tetraphenyl-p-terphenyl (Xd)

A mixture of IX (14.2 g, 20.5 mole), diphenylacetylene (10.7 g, 60.0 mole), and benzophenone (50 g) was heated to a vigorous reflux with a flame. After 10 min. the color faded and heating was continued for an additional 10 min. Diphenyl ether (10 ml) was added to prevent the benzophenone from crystallizing. The reaction mixture was allowed to cool to room temperature and the resultant crystals were collected by filtration and washed with benzene. Yield of Xd: 16 g (86%).

Xd was also prepared in 83% yield by heating the above reactants under reflux in o-dichlorobenzene for 3 days.

Phenylated Dicyano-p-terphenyl Intermediates XIb-d

The following procedure was used to prepare compounds XIb-d.

To a mixture of Xc (100 g, 0.16 mole) and cuprous cyanide (33 g, 0.37 mole) was added dry N-methyl-2-pyrrolidine (800 ml) under a stream of dry nitrogen. After heating under reflux for 20 hr, the hot dark brown mixture was poured into 2 liters of warm water containing 667 g of sodium cyanide. The resulting gray precipitate was washed twice with 10% aqueous sodium cyanide. The solid was air dried at 100°C and then continuously extracted with benzene to give

61 g (74%) of 4,4''-dicyano-2,'3,'5'-triphenyl-p-terphenyl (XIc); mp 305-307°C; ir (KBr) 2200 (C=N); 1670 cm⁻¹ (weak, carboxyl C=O).

Anal. Calcd for C₃₂H₂₀N₂ (XIb): C, 88.86%; H, 4.66%; N, 6.48%. Found: C, 89.11%; H, 4.75%; N, 6.43%.

Calcd for C₃₈H₂₄N₂ (XIc): C, 89.72%; H, 4.75%. Found: C, 89.32%; H, 4.81%.

Calcd for C₄₄H₂₈N₂ (XId): C, 90.38%; H, 4.83%; N, 4.79%. Found: C, 90.39%; H, 4.83%; N, 4.58%.

4,4''-Dicarboxy-2,'3'-diphenyl-p-terphenyl (IVb)

A mixture of XIb (4.6 g, 11 mmole), potassium hydroxide (20 g), and ethylene glycol (190 ml) was heated under reflux for 16 hr. The light orange solution was cooled slightly and 150 ml of water was added. After cooling, the resultant precipitate was collected by filtration, dissolved in hot water, and clarified with activated charcoal, and the solution filtered while hot. The diacid was further purified by dissolving in N,N-dimethylacetamide, treating with charcoal, and precipitating with dilute hydrochloric acid. The white powder (4.70 g, 94%) was washed thoroughly with water and dried at 100°/0.1 torr; mp (DSC) 425°C; ms (70 eV) m/e 470 (M)⁺, 453 (M+H-H₂O)⁺, 427 (M+H-CO₂)⁺; ir (KBr) 1670 cm⁻¹ (C=O).

Anal. Calcd for C₃₂H₂₂O₄: C, 81.68%; H, 4.72%. Found: C, 81.68%; H, 4.44%.

4,4''-Dicarboxy-2,'3,'5'-triphenyl-p-terphenyl (IVc)

A mixture of XIc (50 g, 98 mmole), potassium hydroxide (153 g), and ethylene glycol (1.3 liters) was heated under reflux for 20 hr. The diacid was isolated as described for IVb to give 39 g (72%) of IVc; mp (DSC) 425^o; ms (70 eV) m/e 546 (M)⁺, 529 (M+H-H₂O)⁺, 503 (M+H-CO₂)⁺.

Anal. Calcd for C₃₈H₂₆O₄: C, 83.50%; H, 4.89%. Found: C, 83.41%; H, 4.65%.

4,4''-Dicarboxy-2,'3,'5,'6'-tetraphenyl-p-terphenyl (IVd)

A mixture of XIId (47 g, 70 mmole), potassium hydroxide (98 g), and ethylene glycol (600 ml) was heated under reflux for 20 hr. The diacid was isolated as described for IVb to give 26 g (60%) of IVd; mp: sublimes without melting at 450^oC as shown by DSC; ms (70 eV) m/e 622 (M)⁺.

Anal. Calcd for C₄₄H₃₀O₄: C, 84.87%; H, 4.86%. Found: C, 84.64%; H, 5.00%.

Model Compounds

Pentaphenylphenylbenzoic acid (XIII)

A mixture of tetraphenylcyclopentadienone (5.0 g, 13 mmole), p-phenyl-ethynylbenzoic acid (5.5 g, 25 mmole), and benzophenone (25 g), was heated under reflux for 30 min. Diphenyl ether (7 ml) was added and the mixture allowed to cool. The resultant precipitate was collected by filtration and washed with benzene to give 7.4 g (98%) of XIII; mp > 350^oC; ir (KBr) 1710 (C=O), 730 and 698 cm⁻¹ (5 adjacent aromatic H).

2,6-Bis(2',3',5',6'-tetraphenyl-p-terphenyl)benzo[1,2-d:5,4-d']-bisoxazole (XII)

A mixture of 4,6-diaminoresorcinol dihydrochloride (IIIb) (0.72 g, 3.4 mmole) and freshly prepared PPA (79 g) was heated under a slow stream of nitrogen at 80^oC for 16 hr and then at 110^oC until dehydrochlorination had ceased (8 hr). A mixture of acid XIII (4.30 g, 7.48 mmole) and sulfolane (175 g) was heated to 140^oC and added to the PPA/IIIa mixture. This mixture was heated at 130^oC for 16 hr, at 155^oC for 5 hr, at 185^oC for 2 hr, and finally, at 200 to 205^oC for 1.5 hr. The mixture became homogeneous at 200^oC, and then fine needles crystallized from solution. The mixture was cooled to 160^oC and the precipitate collected by filtration. The fine tan powder was washed with water and dried at 100^oC to give 1.8 g of XII. An additional 1.8 g

was obtained by adding water to the filtrate. Yield: 3.6 g (87%). An analytical sample was obtained by recrystallization from dichloromethane. ν (KBr) 730 and 698 cm^{-1} (5 adjacent H).

Anal. Calcd for $\text{C}_{92}\text{H}_{60}\text{N}_2\text{O}_2$: C, 90.16%, H, 4.93%; N, 2.28%. Found: C, 90.14%; H, 4.90%; N, 1.99%.

Polymers

Polyphosphoric acid (PPA) was prepared immediately before each use by the following method. Phosphorus pentoxide (330 g) was added slowly to 85% phosphoric acid (217 g) while the mixture was stirred under nitrogen and cooled with an ice-water bath. The viscous slurry was then heated with stirring under nitrogen at 150°C for 6 hr to give water-white homogeneous PPA.

The polymers were prepared by adding a stoichiometric quantity of one of the three diacid monomers IV in sulfolane to a dehydrochlorinated mixture of 4,6-diaminoresorcinol dihydrochloride and PPA. The experimental details and characterization are given in Tables 1 and 2. The polymers were isolated by precipitation of the reaction mixture into methanol or water, washing with methanol, air drying, dissolution in methanesulfonic acid, precipitation into methanol, washing with aqueous ammonium hydroxide, and then successive washings with water, methanol, methanol/benzene mixtures, and finally, benzene. The polymers were then freeze-dried from benzene.

Table 1

POLYMER SYNTHESIS AND CHARACTERIZATION

Polymer	Monomers (mmole) ^a	[conc.] ^b	PPA/Sulfolane by weight	Reaction Conditions ^c						[η], dl/g ^d
				hr	°C	hr	°C	hr	°C	
IIb	IIIB (2.811b) + IVb (2.816)	[0.83]	1.2/1	2	130	20	150	1	175	4.91
	IIIB (27.85) + IVb (27.85)	[1.3]	1/1.74	3	120	1	140	1	150	
IIc	IIIB (7.040) + IVc (7.040)	[2.2]	1.6/1	20	135	24	155	24	175	12 195
	IIIB (2.347) + IVc (2.347)	[0.85]	1/1	18	130	5	155	3	185	9.32
	IIIB (49.941) + IVc (49.941)	[1.6]	1/1.3	5	135	16	165	6	190	5.70
IId	IIIB (2.347) + IVd (2.347)	[1.1]	1.1/1	1	120	12	145	2	175	1 210
	IIIB (2.816) + IVb (0.9387) + IVc (0.9387) + IVd (0.9386)	[0.91]	1.6/1	5	135	1	150	1	170	40 185
Copolymers	IIIB (2.347) + IVb (1.1734) + IVc (1.1734)	[0.90]	1.2/1	1	135	1	150	1	170	20 185
										insoluble ^e

^a See experimental section.^b % by wt of monomers in solvent^c Heating schedule after dehydrochlorination of IIIB and addition of IV in sulfolane^d In methanesulfonic acid @ 30°C.^e Monomer IV did not dissolve completely.

Table 2
ELEMENTAL ANALYSIS OF POLYMERS

	Calcd			Found		
	C	H	N	C	H	N
IIb	84.74%	4.12%	5.20%	83.95%	4.01%	-
IIc	85.97	4.26	4.56	85.12	3.59	3.81%
IId	86.93	4.38	4.06	86.53	3.98	-

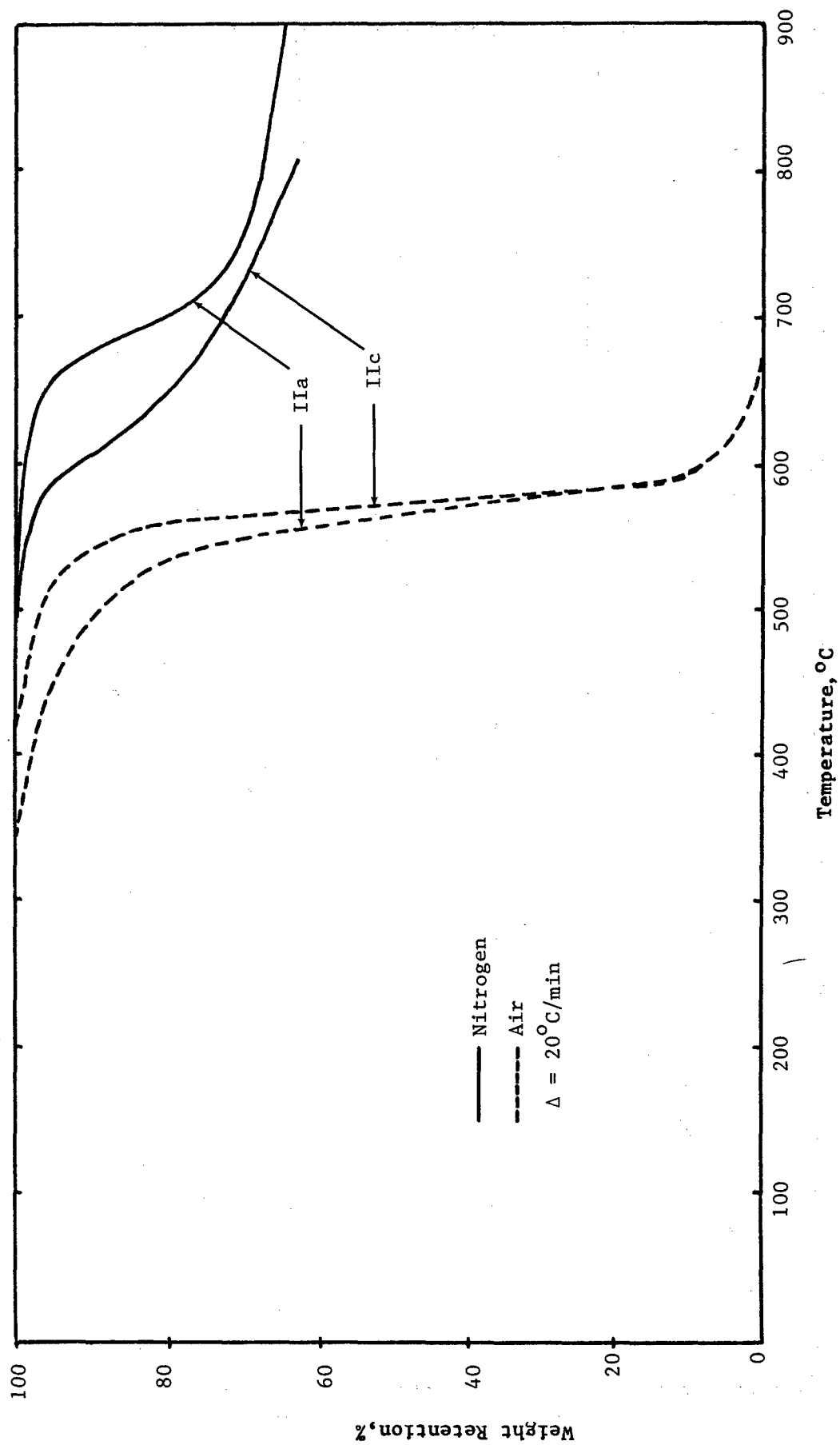


Figure 1. Thermogravimetric Analysis of Polymers IIa and IIc

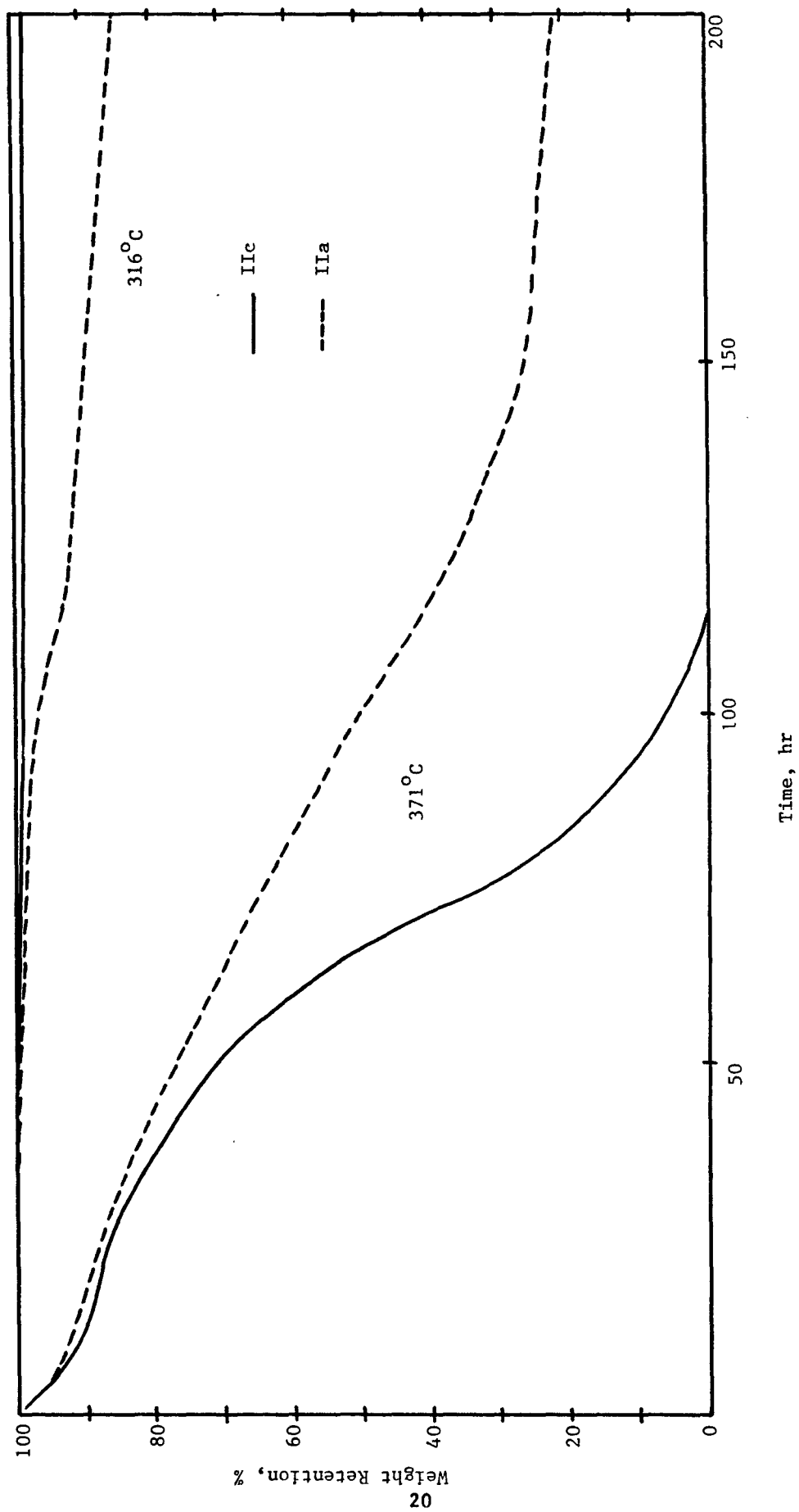


Figure 2. Isothermal Aging in Air at 316°C and 371°C of Polymers IIa and IIc

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